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Probing Radiation Damage in Plutonium Alloys with Multiple Measurement Techniques

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ABSTRACT

A material subjected to radiation damage will usually experience changes in its physical properties. Measuring these changes in the physical properties provides a basis to study radiation damage in a material which is important for a variety of real world applications from reactor materials to semiconducting devices. When investigating radiation damage, the relative sensitivity of any given property can vary considerably based on the concentration and type of damage present as well as external parameters such as the temperature and starting material composition. By measuring multiple physical properties, these differing sensitivities can be leveraged to provide greater insight into the different aspects of radiation damage accumulation, thereby providing a broader understanding of the mechanisms involved. In this report, self-damage from α-particle decay in Pu is investigated by measuring two different properties: magnetic susceptibility and resistivity. The results suggest that while the first annealing stage obeys second order chemical kinetics, the primary mechanism is not the recombination of vacancy-interstitial close pairs.

INTRODUCTION

For most materials, radiation damage results only from external bombardment by a particle beam or flux of electrons, neutrons, or heavier ions. Particularly for the lighter particle irradiations, the damage created consists largely of collections of Frenkel pairs—a vacancy and an interstitial. A second, much less common form of radiation damage is self damage arising from naturally radioactive elements, such as occurs in the actinides. While many of the actinides decay by emission of an α-particle, which approximates a high energy light particle in terms of the damage created, it will also involve the recoil of a heavy ion quite comparable in mass to the other atoms of the lattice. This recoiling ion careens through the lattice like a roller-skating bear in a china shop, initiating dense cascades rich in vacancies and interstitials which are more complex than the relatively dilute concentration of Frenkel pairs created by the α-particle. In the study of radiation damage, radioactive systems have some advantages over those requiring external sources. The damage tends to be uniform and isotropic within the specimen since the decays are equally probable for any atom in the system. This allows samples of any shape to be studied, as well as investigating properties in environments where employing a particle beam is challenging, such as in high magnetic fields, or under high pressure. This makes practical the measurement of some physical properties that are not easily coupled to a particle accelerator, such as magnetization and specific heat.

There are also inherent challenges in studying radioactive specimens. If the sample has an extremely long half life, such as ^{238}U at 4.5 billion years, then the damage will accumulate at a rate so slow as to make experimental measurements time-prohibitive. On the other hand, if the specimen has too short a half life, such as ^{251}Cf at 900 years, it creates difficulties in handling from both its radioactivity and self-heating effects. An ideal material

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for studying radiation damage via self-damage will have a half life between these two materials.

The predominate isotope of Pu is ^{239}Pu, which has a half life of 24,110 years meaning that there are 8.9×10^{11} decays/sec/mol. The principle method of decay is via emission of a 5.16 MeV α–particle along with an 86 keV U ion recoil. The α-particle travels about 10 microns through the lattice losing most of its energy to electronic excitations and collisions. Over the last micron of travel, it begins interacting with the lattice and creates 200-300 isolated Frenkel pairs. The initial cascade resulting from the U deposits its energy into the lattice on a time scale of around 100 fs (1 fs = 10^{-15} s)[2] from which the damage will then evolve depending on the defect concentration and temperature. Molecular dynamics simulations on the fcc δ-Pu structure find that the annealing of the initial damage cascade is hundreds of picoseconds, far longer than typical for fcc metals[3]. Furthermore, this study found that the number of defect pairs surviving the initial cascade strongly depended on contributions from the 5*f* electrons. Thus the damage cascades are significantly more complicated than the classic radiation damage theory of Lindhard-Scharff-Schiott would predict[2, 4].

There have been a series of molecular dynamics simulations, although they are typically run at much lower energies due to the large lattice sizes needed to accommodate 86 keV cascades[5-8]. Most of these simulations are limited to times less than a nanosecond. By contrast, physical property measurements usually require seconds to complete, which are clearly far too slow to observe the initial cascade effects. These measurements are typically made on samples of less than 100 mg, for which there will be $\sim 3.7 \times 10^{8}$ α-particles/second, so even if the collision cascades lasted for a full nanosecond, most of the time nothing would be happening apart from the much slower thermal annealing processes. One way to investigate the initial un-annealed damage cascades is to accumulate them at very low temperatures where the damage is effectively frozen in place after the energy from the initial thermal spike dissipates into the lattice (typically on order of 10 ps). This is the basic idea of isochronal annealing measurements, where radiation damage is accumulated at low temperature ($T \sim 10K$), and then the sample is systematically annealed to higher temperatures while a physical property sensitive to damage is monitored. Different types of radiation damage become mobile at different temperatures, with interstitial motion activated at low temperatures, while vacancy motion is activated at much higher temperatures, and aggregates such as vacancy clusters annealing away only at the highest temperatures. Isochronal annealing measurements can be used to identify the temperatures at which the various annealing stages occur. One frequently monitored physical property is resistivity because of the relative ease of the measurement, and studies have been performed on both α-Pu[9] and more recently on Ga stabilized δ-Pu[10] where several distinct annealing stages are reported. Similar measurements can be made using heat capacity, dilatometry, magnetic susceptibility, etc.

A second type of radiation damage experiment is isothermal annealing, which complements isochronal annealing. While the isochronal annealing studies provide insight as to how temperature influences the evolution of radiation damage, isothermal annealing provides information about how the concentration and type of defects influences annealing properties. Once particular annealing stages have been identified, the chemical kinetics of each annealing stage can be investigated by monitoring a physical property as a function of time while holding the temperature constant. From the time dependence, the order of the

reaction can be determined, thus providing information about how the concentration of defects influences the evolution of radiation damage.

EXPERIMENT

Magnetization measurements were performed using a commercial SQUID magnetometer (Quantum Design MPMS 5) in an applied magnetic field of 3T. Details of the measurement are provided elsewhere[11]. Resistivity measurements were performed on the same specimens that were measured with magnetization. The initial, roughly spherical samples were mechanically rolled, with several intermediate annealing steps to remove strain, until a thickness of 75 microns was obtained. The samples were then laser cut into a cloverleaf pattern and hermetically sealed under a helium atmosphere inside of a copper sample holder with a gold O-ring. A simplified exploded view of the sample holder is shown in Fig. 1, where the sample is shown in red. Non-magnetic spring-loaded pins were mounted in holes drilled through a macor block, and these made electrical contact with the sample. There were two leads on each leaf of the pattern, totaling eight leads. In this configuration, both standard 4-point resistivity and Van der Pauw configurations[12] were available, as was the ability to perform Hall and magnetoresistivity measurements when placed in a magnetic field. A Cernox thermometer was mounted in the middle of the macor block, approximately 1-2 mm from the specimen providing an accurate measure of the sample temperature. The wires for the thermometer and spring loaded pins passed through a small hole in the back of the sample holder which was backfilled with a stycast

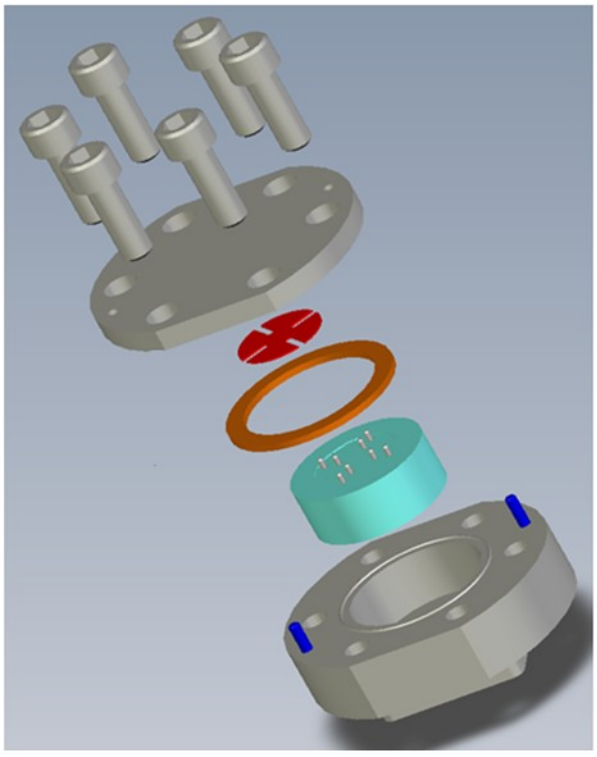

Figure 1 Exploded view of resistivity sample holder for radioactive specimens. The housing is OFHC copper, sealed with a gold O-ring. Inside the housing is the cloverleaf sample (red) and a macor cylinder which centers the 8 spring loaded electrical contacts. The sample rests on a silicon wafer (not shown) to provide electrical insulation from the holder.

epoxy plug. The helium atmosphere provided good thermal communication between the sample and thermometer over the entire temperature range from 2-370 K. The entire sample holder was then coated with polyimide to form a second layer of encapsulation. Measurements were made using a commercial 16T magnet/cryostat with a resistance bridge (Quantum Design PPMS).

As with the magnetization measurements, samples were held at low temperatures for extended periods of time to study the effects of radiation damage accumulation on the physical properties of δ-Pu. Damage was accumulated below 25 K, and then isochronal annealing curves were obtained.

DISCUSSION

Radiation damage in metals has a measurable effect on many physical properties and monitoring the change in these properties can provide insight into the nature of radiation damage. Some properties, such as resistivity, should be sensitive to all types of radiation damage, where each defect can be considered as an impurity that increases the scattering rate, thereby increasing the resistivity of the sample. In this situation, the change in resistivity as a function of damage (or time for radioactive specimens) will behave like:

(1)

where $\rho_o(T)$ is the temperature dependence of the undamaged specimen, while $n_j(t)$ and $\rho_j(T)$ are the defect concentration and the specific resistivity for the j^{th} type of defect, respectively, be it a vacancy, interstitial, etc. The increase in resistivity arises from increased scattering by the defects, and thus will be independent of temperature, i.e. $\rho_j(T) = \rho_j$.

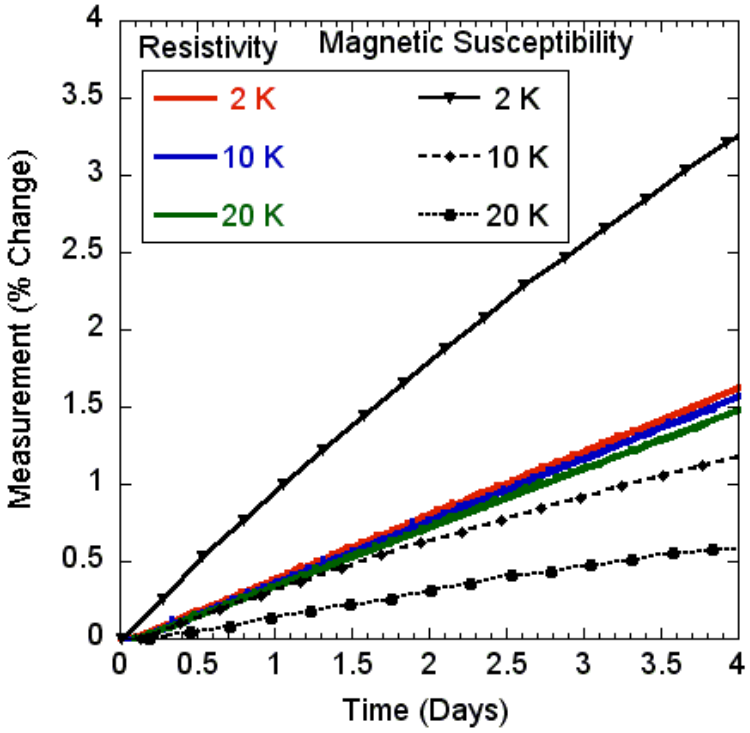

Fig. 2 Change of two physical properties due to radiation damage. The change in resistivity is temperature independent, with the slight variation due to the normalization resulting from the temperature dependence of the undamaged contribution

On the other hand, the basis for increasing the magnetic susceptibility through radiation damage is not a priori obvious. However, the functional form should be substantially equivalent to eqn (1):

(2)

where $\chi_j(T)$ is the specific magnetic susceptibility of the j^{th} type of defect. Investigation of the low temperature properties of Pu has shown that the total specific magnetic susceptibility of the defects has a Curie-Weiss temperature dependence ($\chi \sim 1/T$)[1, 13, 14]. It has been argued that radiation damage is either creating or uncovering local magnetic moments in Pu which may be shielded by screening in the undamaged lattice[15].

The relative sensitivity of these techniques is illustrated in Fig. 2 for both types of measurements at several different temperatures. The temperature dependence of the defect specific magnetic susceptibility makes it a poor probe at even modest temperatures (> 30K). By contrast, the temperature independence of the defect specific resistivity makes it a useful probe for a wide range of temperatures. The variation in the percent change with time in the resistivity measurement is due to slightly different normalization factors from the temperature dependence of the undamaged material—the absolute change is constant within the uncertainty of the measurement. An additional feature notable in Fig. 2 is the strong linearity of the resistivity measurements while all of the magnetic susceptibility measurements demonstrate curvature suggesting they will saturate, with a time constant of about 11 days when fit to a [1-exp(-t/τ)] time dependence[1]. Earlier work on resistivity for samples of α-Pu held at cryogenic temperatures for much longer time periods find a similar behavior, but with a much longer time constant of roughly 64 days[16]. Since the magnetic susceptibility is a bulk measurement, this behavior can be attributed to overlapping regions of damage, from which a volume estimate per cascade can be extracted. Resistivity is a transport measurement, which measures the path of least resistance for the sample. This will vary depending on the specific resistivity of defects as compared to the undamaged region and their location in the sample, since the current path will

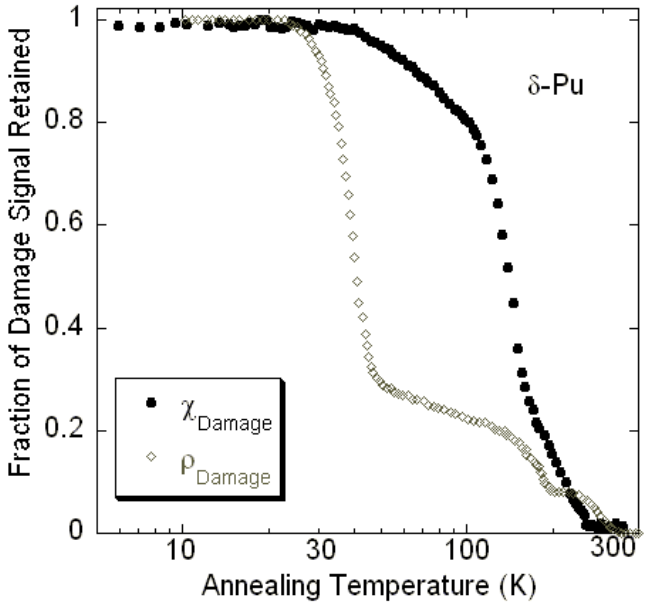

Fig. 3 Isochronal annealing curves measured with magnetic susceptibility and resistivity for Ga stabilized δ-Pu specimens (from [13]).

also change as regions of higher resistivity are created. Thus, there is no simple model to estimate cascade sizes for this measurement.

Isochronal annealing curves obtained using both resistivity and magnetic susceptibility measurements are shown in Fig. 3 for Ga stabilized δ-Pu. The resistivity isochronal annealing curve shows a large change in the fraction of the damage signal retained just below 50 K, where roughly 70% of the resistance is annealed away. By contrast, the isochronal annealing curve for the magnetic susceptibility on the same sample shows essentially no annealing below 50 K, and has only annealed away about 20% of its signal by 100 K[1]. From these two very different curves, it is evident that the fractional change in the signal is not necessarily proportional to the total damage annealed. Each technique has differing sensitivity to different types of damage. By itself, the resistivity data indicates Stage I annealing where interstitials begin to move, and close vacancy-interstitial pairs annihilate. By contrast, the magnetic susceptibility isochronal annealing curve shows a strong reduction where the resistivity data suggests Stage III annealing—the temperature where vacancies begin to move. This implies that the magnetic measurement is insensitive to interstitials. If this is true, then the absence of Stage I annealing observed in this measurement suggests that it does not involve a significant fraction of interstitial-vacancy recombination.

Preliminary results of resistivity based isothermal annealing are shown in Fig. 4 for a specimen held at 45K, which is the temperature where the interstitials are believed to begin moving. The red data are the actual measured resistance as a function of time over the course of two days, while the blue data are corrected for the radiation damage accumulated during the isothermal hold. The correction comes from a linear fit to the measured resistance for the last 10 hours of data accumulation. The inset shows that $(1/\Delta R)$ is linear in time, which is consistent with 2nd order kinetics based on the rate equation: $dp = -Kp^{\gamma}dt$, where p is the property being

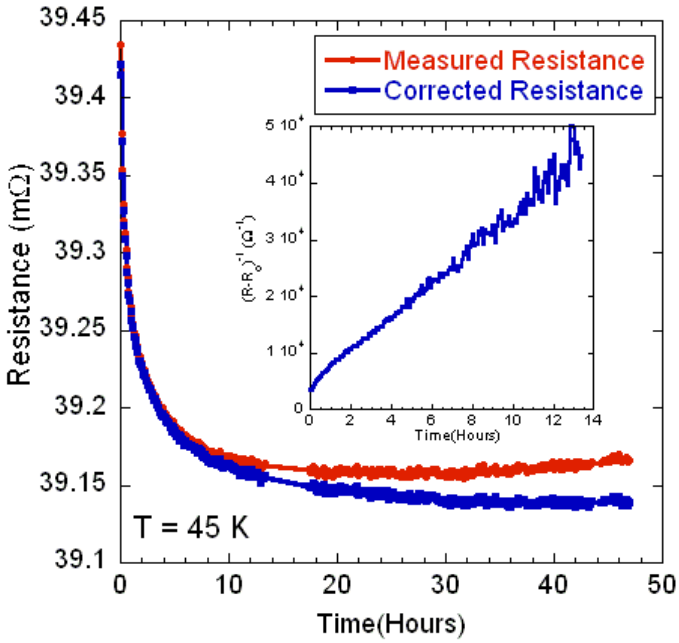

Fig.4 Isothermal annealing curve showing the measured resistance and the resistance corrected for the additional damage accumulated while holding the sample at 45K. The inset shows that the inverse of the change in resistance is proportional to time, indicating 2nd order kinetics are involved.

measured, K is a rate constant, and γ is the order of the kinetics. The first mechanism that might spring to mind for a second order reaction would be recombination of interstitial-vacancy close pairs. But as described above, this is not consistent with the observed isochronal annealing data of the magnetic susceptibility measurement. A second possible mechanism is clustering of interstitials into more complicated structures such as dislocation loops. It is possible that this stage is actually driven by the damage process itself where interstitials interact directly with the new damage cascades that are continuously erupting. While unexpected, such behavior could be tested for by performing isochronal annealing measurements on an alloy spiked with ^{238}Pu.

CONCLUSIONS

Radiation damage can be probed by a variety of physical property measurements. Combining multiple measurement techniques that have differing sensitivity to various defects provides greater insight into the damage cascade. Radiation damage in δ-Pu was studied by a combination of magnetic susceptibility and resistivity techniques. The observations suggest that the first annealing stage is not dominated by vacancy-interstitial recombination, but by a different 2nd order reaction perhaps based on interstitials and their aggregates.

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